16.4 Integrated Rate Laws

- Give the concentration of the reactants as a function of time

Zero order reactions

General reaction: **A → Products** (Zero-order)

$\rightarrow$ ***Rate*** $= k$ and ***Rate*** $= -\Delta[A]/\Delta t$

$-\Delta[A]/\Delta t = k$ → **Differential** rate law (zero-order)

- Integration of the differential equation leads to:

$\boxed{[A] = [A]_o - kt}$ → **Integrated** rate law (zero-order)

- Gives the concentration of the reactant **[A]** at time ***t*** during the reaction
- $[A]_o$ is the initial concentration at time $t = 0$

First order reactions

General reaction: **A → Products** (1st order)

$\rightarrow$ ***Rate*** $= k[A]$ and ***Rate*** $= -\Delta[A]/\Delta t$

$-\Delta[A]/\Delta t = k[A]$ → **Differential** rate law (1st order)

- Integration of the differential equation leads to:

$\boxed{[A] = [A]_o e^{-kt}}$ → **Integrated** rate law (1st order)
→ Exponential form

- Take a natural logarithm of both sides:

$\boxed{\ln[A] = \ln[A]_o - kt}$ → Logarithmic form

- Gives the concentration of the reactant **[A]** at time ***t*** during the reaction
- $[A]_o$ is the initial concentration at time $t = 0$

Second order reactions

General reaction: **A → Products** (2nd order)

$\rightarrow$ ***Rate*** $= k[A]^2$ and ***Rate*** $= -\Delta[A]/\Delta t$

$-\Delta[A]/\Delta t = k[A]^2$ → **Differential** rate law (2nd order)

- Integration of the differential equation leads to:

$\boxed{1/[A] = 1/[A]_o + kt}$ → **Integrated** rate law (2nd order)

Example: For a given **zero-order** reaction the rate constant is **0.011 M/s** at 25°C. If the initial concentration of the reactant is **1.4 M**, what is its concentration after **1.5 minutes**?

$[A] = [A]_o - kt = 1.4\ \mathrm{M} - 0.011\ \mathrm{M}/\cancel{\mathrm{s}} \times 90\ \cancel{\mathrm{s}} = 0.4\ \mathrm{M}$

Example: The decomposition of HI at 25°C is a **2nd order** reaction with a rate constant of **2.4×10^{-21} L/mol·s**. If the initial concentration of HI is **0.050 M**, how long would it take for **30%** of it **to react**?

- $2HI \rightarrow H_2 + I_2 \rightarrow Rate = k[HI]^2 \rightarrow$ 2nd order
- 30% HI reacted ↔ 70% HI remaining

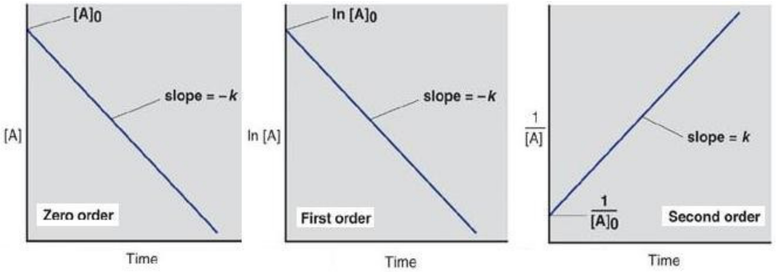
$\Rightarrow [HI]_o = 0.050\ \mathrm{M} \qquad [HI] = 0.70\times0.050 = 0.035\ \mathrm{M}$

$\rightarrow 1/[HI] = 1/[HI]_o + kt \quad \rightarrow \quad 1/[HI] - 1/[HI]_o = kt$

$\rightarrow t = (1/[HI] - 1/[HI]_o)/k$

$$t = \frac{\left(\dfrac{1}{0.035\,\cancel{\mathrm{mol}}/\cancel{\mathrm{L}}} - \dfrac{1}{0.050\,\cancel{\mathrm{mol}}/\cancel{\mathrm{L}}}\right)}{2.4\times10^{-21}\ \cancel{\mathrm{L}}/\cancel{\mathrm{mol}}\cdot\mathrm{s}} = 3.6\times10^{21}\,\mathrm{s} = 1.1\times10^{14}\,\mathrm{yr}$$

- Graphical representation of integrated rate laws



$[A] = [A]_o - kt$
$y \;=\; b \;+\; mx$
⇒ If a plot of **[A] versus time** gives a straight line, the reaction is **zero-order** in A

$\ln[A] = \ln[A]_o - kt$
$y \;=\; b \;+\; mx$
⇒ If a plot of **ln[A] versus time** gives a straight line, the reaction is **1st order** in A

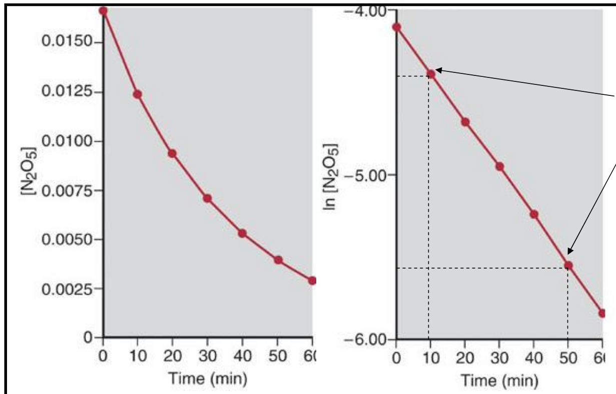
$1/[A] = 1/[A]_o + kt$
$y \;=\; b \;+\; mx$
⇒ If a plot of **1/[A] versus time** gives a straight line, the reaction is **2nd order** in A

Example: Determine the reaction order and the rate constant for the decomposition of N_2O_5 from the following data: $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

Time (min)	$[N_2O_5]$	$\ln[N_2O_5]$	$1/[N_2O_5]$
0	0.0165	−4.104	60.6
10	0.0124	−4.390	80.6
20	0.0093	−4.68	1.1×10^2
30	0.0071	−4.95	1.4×10^2
40	0.0053	−5.24	1.9×10^2
50	0.0039	−5.55	2.6×10^2
60	0.0029	−5.84	3.4×10^2

← Calculate $\ln[N_2O_5]$ and $1/[N_2O_5]$

→ Using a trail-and-error approach, plot $[N_2O_5]$, $\ln[N_2O_5]$, and $1/[N_2O_5]$ versus time until a straight line is obtained



(10.0, -4.39)

(50.0, -5.55)

k = -slope
$k = -\Delta y/\Delta x$

→ A plot of **$[N_2O_5]$** versus ***t*** is not a straight line ⇒ reaction is not zero-order

→ A plot of **$\ln[N_2O_5]$** versus ***t*** gives a straight line ⇒ reaction is **1st order**

$$-\frac{[-5.55 - (-4.39)]}{(50.0 - 10.0)}$$

$$k = 0.029 \text{ min}^{-1}$$

Reaction Half-Life

- **Half-life ($t_{1/2}$)** – the time needed to reduce the reactant concentration to ½ of its initial value

➢ **$t_{1/2}$ for 1st order** reactions

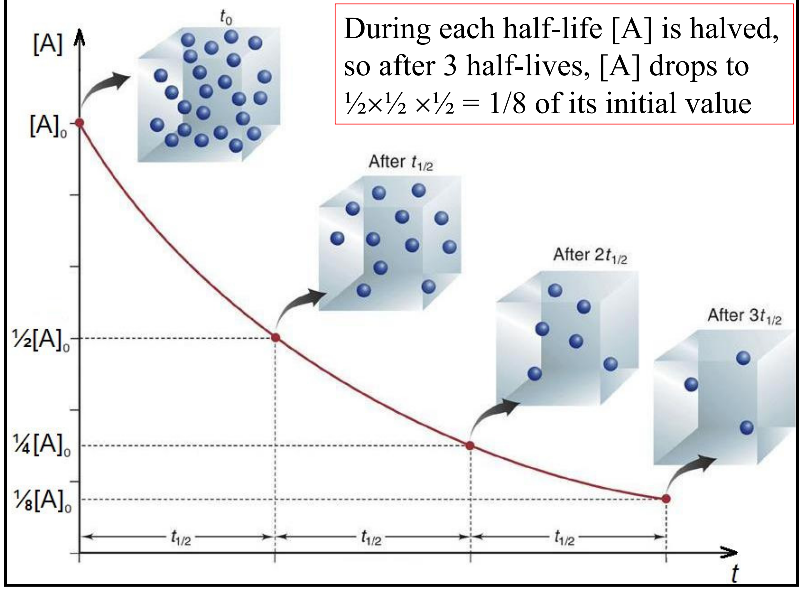
$$\rightarrow [A] = [A]_o e^{-kt} \quad \rightarrow \quad \tfrac{1}{2}\cancel{[A]_o} = \cancel{[A]_o} e^{-kt_{1/2}}$$

$$\rightarrow \ln(\tfrac{1}{2}) = -kt_{1/2} \quad \rightarrow \quad \ln(2) = kt_{1/2}$$

$$\boxed{t_{1/2} = \ln(2)/k = 0.693/k}$$

⇒ $t_{1/2}$ is independent of the initial concentration **$[A]_o$**

⇒ During the course of the reaction, $t_{1/2}$ remains the same, so it always takes the same time to half **[A]**



During each half-life [A] is halved, so after 3 half-lives, [A] drops to $\frac{1}{2}\times\frac{1}{2}\times\frac{1}{2} = 1/8$ of its initial value

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- $t_{1/2}$ for **zero-order** reactions

→ $[A] = [A]_0 - kt$ → $\frac{1}{2}[A]_0 = [A]_0 - kt_{1/2}$

→ $kt_{1/2} = [A]_0 - \frac{1}{2}[A]_0$ → $kt_{1/2} = \frac{1}{2}[A]_0$

$$\boxed{t_{1/2} = [A]_0/2k}$$

⇒ $t_{1/2}$ is directly proportional to $[A]_0$

- $t_{1/2}$ for 2nd **order** reactions

→ $1/[A] = 1/[A]_0 + kt$ → $1/\frac{1}{2}[A]_0 = 1/[A]_0 + kt_{1/2}$

→ $2/[A]_0 - 1/[A]_0 = kt_{1/2}$ → $1/[A]_0 = kt_{1/2}$

$$\boxed{t_{1/2} = 1/k[A]_0}$$

⇒ $t_{1/2}$ is inversely proportional to $[A]_0$

- Radioactive decay is a 1st order process

Example: $t_{1/2}$ is **5700 yr** for the radioactive isotope of carbon, ^{14}**C**. **C**-dating shows that the concentration of ^{14}**C** in an object has decreased to **25%** of its original value. How old is the object?

→ $t_{1/2} = 0.693/k$ → $k = 0.693/t_{1/2} = 0.693/5700\ \text{yr}$

→ $k = 1.21\times10^{-4}\ \text{yr}^{-1}$

→ $[^{14}C] = [^{14}C]_0 e^{-kt}$ → $[^{14}C] = 0.25[^{14}C]_0$

→ $0.25[^{14}C]_0 = [^{14}C]_0 e^{-kt}$ → $0.25 = e^{-kt}$

→ $\ln(0.25) = -kt$ → $t = -\ln(0.25) / k$

→ $t = -\ln(0.25) / 1.21\times10^{-4}\ \text{yr}^{-1} = \boxed{11{,}000\ \text{yr}}$